

Claims

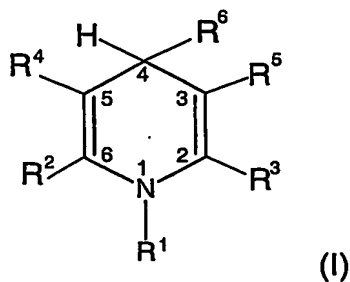
1. Radiation-sensitive composition comprising

- (a) at least one photopolymerizable compound with at least one ethylenically unsaturated group accessible to a free-radical polymerization, wherein the at least one photopolymerizable compound has a molecular weight of 3,000 or less and can be obtained by reacting a diisocyanate with (i) an ethylenically unsaturated compound with a hydroxy group, and at the same time (ii) a saturated organic compound with an NH group and an OH group, wherein the reactants are used in amounts according to the following condition:

Number of moles of isocyanate groups \leq number of moles of OH plus NH groups;

- (b) at least one sensitizer which absorbs radiation from the wavelength range of 250 to 450 nm of the electromagnetic spectrum and is selected from:

- (i) a 1,4-dihydropyridine derivative of formula (I)



wherein

R¹ is selected from a hydrogen atom, -C(O)OR⁷, an optionally substituted alkyl group, an optionally substituted aryl group and an optionally substituted aralkyl group,

R² and R³ are independently selected from optionally substituted alkyl groups, optionally substituted aryl groups, CN and a hydrogen atom,

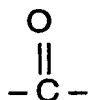
R⁴ and R⁵ are independently selected from -C(O)OR⁷, -C(O)R⁷, -C(O)NR⁸R⁹ and CN,

or R² and R⁴ together form an optionally substituted phenyl ring or a 5- to 7-membered carbocyclic or heterocyclic ring, wherein the unit



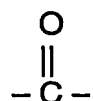
is present in the carbocyclic or heterocyclic ring adjacent to position 5 of the 1,4-dihydropyridine ring and wherein the carbocyclic or heterocyclic ring optionally comprises additional substituents,

or both R² and R⁴ as well as R³ and R⁵ form either optionally substituted phenyl rings or 5- to 7-membered carbocyclic or heterocyclic rings, wherein the unit



is present in the carbocyclic or heterocyclic rings adjacent to positions 3 and 5 of the dihydropyridine ring and wherein the carbocyclic or heterocyclic rings optionally comprise additional substituents,

or one of the pairs R²/R⁴ and R³/R⁵ forms a 5- to 7-membered carbocyclic or heterocyclic ring, wherein the unit

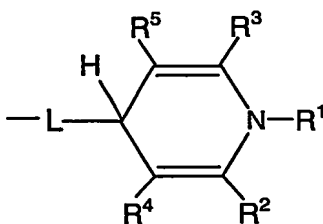


is present in the carbocyclic or heterocyclic ring adjacent to position 5 or 3 of the dihydropyridine ring and wherein the carbocyclic or heterocyclic ring optionally comprises additional substituents and the other pair forms an optionally substituted phenyl ring,

or R^2 and R^1 or R^3 and R^1 form a 5- to 7-membered heterocyclic ring which can optionally comprise one or more substituents and which, in addition to the nitrogen atom it shares with the 1,4-dihydropyridine ring, optionally comprises additional nitrogen atoms, $-NR^{13}$ groups, $-S-$ or $-O-$,

R^{13} is selected from a hydrogen atom, an alkyl group, aryl group and aralkyl group,

R^6 is selected from an alkyl group optionally substituted with a halogen atom or a $-C(O)$ group, an optionally substituted aryl group, an optionally substituted aralkyl group, an optionally substituted heterocyclic group and the group



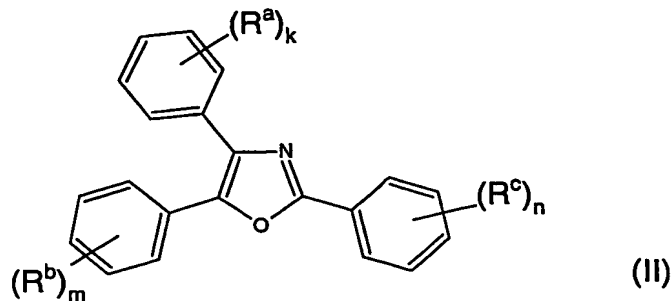
wherein

L is an alkylene or arylene group and R^1 to R^5 are as defined above for formula (I),

R^7 is a hydrogen atom, aryl group, aralkyl group or alkyl group, wherein the alkyl group and the alkyl unit of the aralkyl group optionally comprise one or more C-C double and/or C-C triple bonds, and

R^8 and R^9 are independently selected from a hydrogen atom, an optionally substituted alkyl group, an optionally substituted aryl group and an optionally substituted aralkyl group; and

(ii) an oxazole compound of formula (II)



wherein each R^a , R^b and R^c is independently selected from a halogen atom, an optionally substituted alkyl group, an optionally substituted aryl group, which may also be fused, an optionally substituted aralkyl group, a group $-NR'R''$ and a group $-OR'''$,

wherein R' and R'' are independently selected from a hydrogen atom, an alkyl, aryl or aralkyl group,

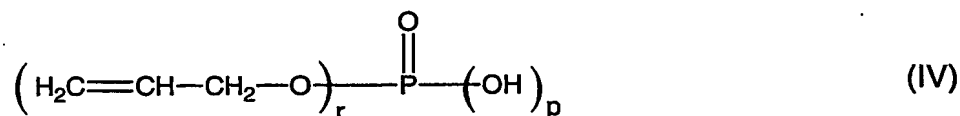
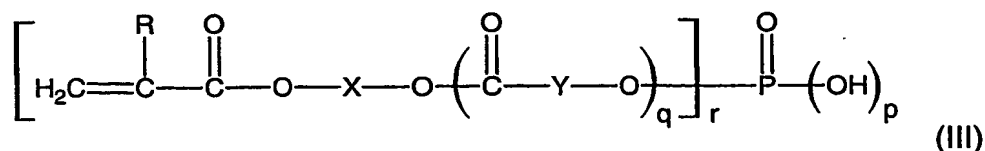
R''' is an optionally substituted alkyl, aryl or aralkyl group or a hydrogen atom and

k , m and n are independently 0 or an integer from 1 to 5;

- (c) at least one coinitiator capable of forming free radicals together with the sensitizer (b) and selected from 2,2',4,4',5,5'-hexaarylbiimidazoles, compounds with at least one photolytically cleavable trihalogenmethyl group, diaryliodonium salts, triarylsulfonium salts and N-heterocyclic compounds with at least one nitrogen atom in the ring, having an oxy substituent at at least one ring nitrogen atom, and mixtures of the above compounds; and
- (d) optionally one or more components selected from alkali-soluble binders, colorants, exposure indicators, plasticizers, chain transfer agents, leuco dyes, surfactants, inorganic fillers and thermopolymerization inhibitors;

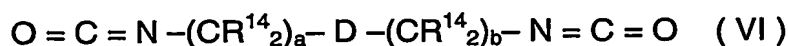
with the proviso that the radiation-sensitive composition does not comprise a metallocene.

2. Radiation-sensitive composition according to claim 1, wherein a hexaarylbiimidazole is used as coinitiator.
3. Radiation-sensitive composition according to claim 1 or 2, additionally comprising at least one component with at least one ethylenically unsaturated free-radical polymerizable group and at least one P-OH group.
4. Radiation-sensitive composition according to claim 3, wherein the component with the ethylenically unsaturated group and the P-OH group is a compound of formula (III) or (IV):



wherein r is 1 or 2, q is 0 or 1, p is 1 or 2, $r+p=3$, R represents $\text{C}_1\text{-C}_{12}$ alkyl, X represents $\text{C}_2\text{-C}_{12}$ alkylene and Y is $\text{C}_2\text{-C}_{12}$ alkylene.

5. Radiation-sensitive composition according to any of claims 1 to 4, wherein the diisocyanate is a compound of formula (VI)

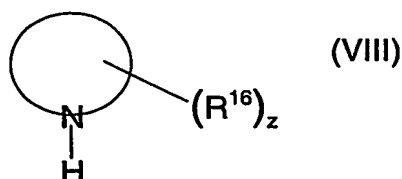
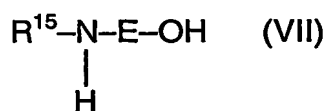


wherein a and b independently represent 0 or an integer from 1 to 3, each R^{14} is independently selected from H and $\text{C}_1\text{-C}_3$ alkyl and D is a saturated or unsaturated, chain-shaped or ring-shaped spacer.

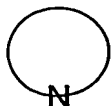
6. Radiation-sensitive composition according to any of claims 1 to 5, wherein the ethylenically unsaturated compound with a hydroxy group is at least one compound selected from

hydroxy(C₁-C₁₂)alkyl(meth)acrylates,
 hydroxy(C₁-C₁₂)alkyl(meth)acrylamides,
 mono(meth)acrylates of oligomeric or polymeric ethylene glycols or propylene glycols,
 allyl alcohol,
 pentaerythritol tri(meth)acrylate,
 4-hydroxy(C₁-C₁₂)alkylstyrene,
 4-hydroxystyrene and
 hydroxycyclohexyl(meth)acrylate.

7. Radiation-sensitive composition according to any of claims 1 to 6, wherein the saturated compound with an NH group and an OH group is a compound of formula VII or VIII or a mixture thereof:



wherein R¹⁵ is a straight-chain, branched or cyclic alkyl group,
 E is a straight-chain, branched or cyclic alkylene group,

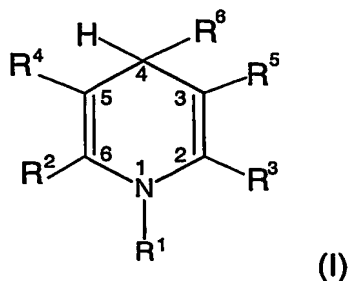


represents a saturated heterocyclic ring with 5 to 7 ring atoms, which optionally comprises an additional heteroatom selected from S, O and NR¹⁷,
 R¹⁶ is OH or an alkyl group substituted with an OH group,
 R¹⁷ is an alkyl group optionally substituted with an OH group,
 z = 0 if the heterocyclic ring comprises NR¹⁷ and R¹⁷ is an alkyl group substituted with OH and
 z = 1 if the heterocyclic ring does not comprise NR¹⁷ or if the heterocyclic ring comprises NR¹⁷ and R¹⁷ is an unsubstituted alkyl group.

8. Radiation-sensitive composition according to any of claims 1 to 7, wherein the diisocyanate is selected from hexamethylene diisocyanate and trimethylhexamethylene diisocyanate, the ethylenically unsaturated compound (i) is selected from esters of (meth)acrylic acid with an at least divalent alcohol, and the compound (ii) is selected from piperidines and piperazines comprising an OH group bonded directly or via a spacer.
9. Radiation-sensitive composition according to any of claims 1 to 8, additionally comprising one or more chain transfer agents.
10. Negative working radiation-sensitive element comprising
 - (a) an optionally pretreated substrate and
 - (b) a radiation-sensitive coating prepared from the composition as defined in any of claims 1 to 9 applied onto the substrate.
11. Negative working radiation-sensitive element according to claim 10, wherein the substrate is an aluminum foil or plate.
12. Negative working radiation-sensitive element according to claim 11, wherein prior to coating the aluminum plate or foil was subjected to at least one treatment selected from graining, anodizing and hydrophilizing.
13. Negative working radiation-sensitive element according to any of claims 10 to 12, wherein the element furthermore comprises an oxygen-impermeable overcoat layer.
14. Process for imaging a radiation-sensitive element comprising
 - (a) providing a negative working radiation-sensitive element as defined in any of claims 10 to 13;

- (b) image-wise irradiation of the element with UV radiation of a wavelength in the range of 250 to 450 nm;
 - (c) optionally heating of the image-wise irradiated element;
 - (d) removing the non-irradiated areas of the coating by means of an aqueous alkaline developer;
 - (e) optionally heating the developed element and/or subjecting it to overall exposure.
15. Process according to claim 14, wherein the image-wise irradiation is carried out with UV radiation of a wavelength in the range of 400 to 450 nm.
16. Imaged element obtainable according to the process of claim 14 or 15.
17. Imaged element according to claim 16, wherein the element is a lithographic printing form.
18. Process for the production of a radiation-sensitive element comprising
- (a) providing an optionally pretreated substrate,
 - (b) providing a radiation-sensitive composition comprising
 - (i) at least one photopolymerizable compound as defined in any of claims 1, 5, 6, 7 or 8;
 - (ii) at least one sensitizer which absorbs radiation from the wavelength range of 250 to 450 nm of the electromagnetic spectrum and is selected from:

a 1,4-dihydropyridine derivative of formula (I)



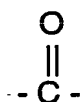
wherein

R^1 is selected from a hydrogen atom, $-C(O)OR^7$, an optionally substituted alkyl group, an optionally substituted aryl group and an optionally substituted aralkyl group,

R^2 and R^3 are independently selected from optionally substituted alkyl groups, optionally substituted aryl groups, CN and a hydrogen atom,

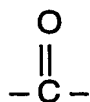
R^4 and R^5 are independently selected from $-C(O)OR^7$, $-C(O)R^7$, $-C(O)NR^8R^9$ and CN,

or R^2 and R^4 together form an optionally substituted phenyl ring or a 5- to 7-membered carbocyclic or heterocyclic ring, wherein the unit



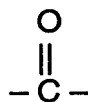
is present in the carbocyclic or heterocyclic ring adjacent to position 5 of the 1,4-dihydropyridine ring and wherein the carbocyclic or heterocyclic ring optionally comprises additional substituents,

or both R^2 and R^4 as well as R^3 and R^5 form either optionally substituted phenyl rings or 5- to 7-membered carbocyclic or heterocyclic rings, wherein the unit



is present in the carbocyclic or heterocyclic rings adjacent to positions 3 and 5 of the dihydropyridine ring and wherein the carbocyclic or heterocyclic rings optionally comprise additional substituents,

or one of the pairs R^2/R^4 and R^3/R^5 forms a 5- to 7-membered carbocyclic or heterocyclic ring, wherein the unit

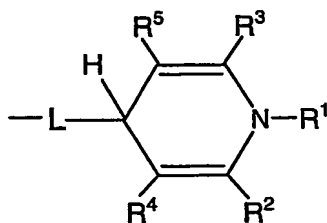


is present in the carbocyclic or heterocyclic ring adjacent to position 5 or 3 of the dihydropyridine ring and wherein the carbocyclic or heterocyclic ring optionally comprises additional substituents and the other pair forms an optionally substituted phenyl ring,

or R^2 and R^1 or R^3 and R^1 form a 5- to 7-membered heterocyclic ring which can optionally comprise one or more substituents and which, in addition to the nitrogen atom it shares with the 1,4-dihydropyridine ring, optionally comprises additional nitrogen atoms, $-NR^{13}$ groups, $-S-$ or $-O-$,

R^{13} is selected from a hydrogen atom, an alkyl group, aryl group and aralkyl group,

R^6 is selected from an alkyl group optionally substituted with a halogen atom or a $-C(O)$ group, an optionally substituted aryl group, an optionally substituted aralkyl group, an optionally substituted heterocyclic group and the group



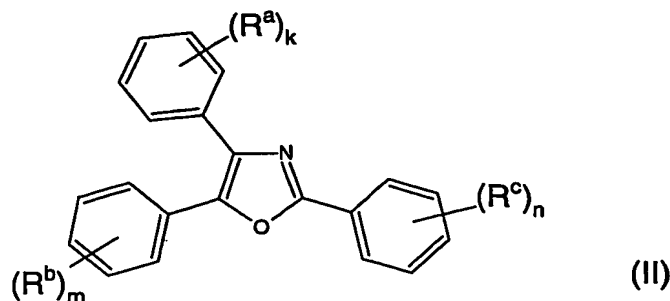
wherein

L is an alkylene or arylene group and R^1 to R^5 are as defined above for formula (I),

R^7 is a hydrogen atom, aryl group, aralkyl group or alkyl group, wherein the alkyl group and the alkyl unit of the aralkyl group optionally comprise one or more C-C double and/or C-C triple bonds, and

R^8 and R^9 are independently selected from a hydrogen atom, an optionally substituted alkyl group, an optionally substituted aryl group and an optionally substituted aralkyl group

and an oxazole compound of formula (II)



wherein each R^a , R^b and R^c is independently selected from a halogen atom, an optionally substituted alkyl group, an optionally substituted aryl group, which may also be fused, an optionally substituted aralkyl group, a group $-NR'R''$ and a group $-OR'''$,

wherein R' and R'' are independently selected from a hydrogen atom, an alkyl, aryl or aralkyl group,

R''' is an optionally substituted alkyl, aryl or aralkyl group or a hydrogen atom and

k , m and n are independently 0 or an integer from 1 to 5;

- (iii) at least one coinitiator capable of forming free radicals together with the sensitizer (b) and selected from 2,2',4,4',5,5'-hexaarylbiimidazoles, compounds with at least one photolytically cleavable trihalogenmethyl group, diaryliodonium salts, triarylsulfonium salts and N-heterocyclic compounds with at least one nitrogen atom in the ring, having an oxy substituent at at least one ring nitrogen atom, and mixtures of the above compounds;
- (iv) optionally one or more components selected from alkali-soluble binders, colorants, exposure indicators, plasticizers, chain transfer agents, leuco dyes, surfactants, inorganic fillers and thermopolymerization inhibitors, and

(v) at least one solvent,

with the proviso that the radiation-sensitive composition does not comprise a metallocene;

c) applying the radiation-sensitive composition onto the substrate;

d) drying.

19. Process according to claim 18, wherein the substrate provided in step (a) is an aluminum substrate that has been subjected to at least one treatment selected from graining, anodizing and hydrophilizing.
20. Use of a radiation-sensitive composition as defined in any of claims 1 to 9 for producing a lithographic printing plate precursor.